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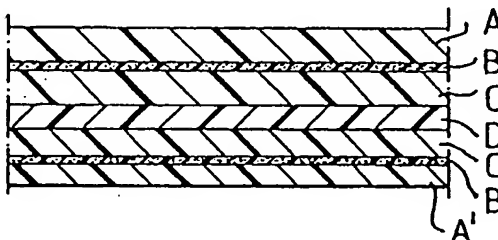
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(21) International Application Number: PCT/SE94/00138 (22) International Filing Date: 18 February 1994 (18.02.94) (30) Priority Data: 9300558-5 19 February 1993 (19.02.93) SE (71) Applicants (for all designated States except US): KABI PHARMACIA AB [SE/SE]; S-751 82 Uppsala (SE). WIHURI OY WIPAK [FI/FI]; P.O. Box 45, SF-15561 Nastola (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): HÖGSTRÖM, Peter [SE/SE]; Hallandsgatan 44, S-118 57 Stockholm (SE). LUNDMARK, Stefan [SE/SE]; Kungshatt 163 C, S-178 93 Drottningholm (SE). LINDHE, Curt [SE/SE]; Mårtsbo, P.L. 5011, S-770 20 Söderbärke (SE). MAASOLA, Hannu [FI/FI]; Leivonpolku 10, SF-155 40 Villähde (FI). (74) Agents: FORSLUND, Niklas et al.; Kabi Pharmacia AB, S-112 87 Stockholm (SE).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.	

(54) Title: AUTOCLAVABLE MULTILAYER FILMS

(57) Abstract

An autoclavable, transparent multilayer film with oxygen barrier capacity assembled of thermoplastic materials, capable of being processed into hollow shapes and useful for the packaging of oxygen sensitive goods. The film is assembled in sequential layers A-B-C-D-C-B'-A' wherein A and A' are layers substantially resistant for water and water vapor;

B and B' are layers providing adhesive bondings between layers A and A' with C; C is a layer of a moisture absorbing polymer substantially impermeable for oxygen which contains an aromatic polyamide or a derivate or a copolymer thereof; D is a layer consisting of polyethylene-vinylalcohol (EVOH) with a molar ethene concentration between 0-80 %.



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## Autoclavable multilayer films

### Field of invention

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The present invention relates to novel autoclavable multilayer films of polymeric materials, packages and flexible containers made thereof as well as a process for the production of such articles and the use of the films.

The articles made from the novel multilayer films are especially suitable to contain oxygen sensitive medical or nutritional fluids for parenteral or enteral administration, because they retain both their transparency and oxygen barrier properties after autoclavation.

### Background of the invention

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It has been a considerable technical problem for manufacturers of materials for medical containers or packages to provide an autoclavable material compatible with infusion fluids often containing fat emulsions, to be administrated parenterally. Especially flexibility and transparency of the material is desirable to retain after the autoclavation in the same time as the it meets the demand of having an oxygen and water barrier for the protection of sensitive contents during storage.

Another problem to be solved is to find a polymer material which fulfils these criteria and still is environmental friendly and without any hazards for the manufacturers.

In many medical materials polymer materials such as those prepared from halogenated hydrocarbons like PVC or PVDC have traditionally been used, since they often have low permeability for water and gases and have advantageous mechanical properties. Medical plastic bags made from PVC are, however, undesirable because medical fluids may dissolve softeners from the PVC, making them incompatible with many requirements in pharmaceutical applications. Such migration effects can be especially problematic when storing fat emulsions which tend dissolve hydrophobic components from the polymers. PVC and other polymers from halogenated hydrocarbons are also unsuitable for other technical reasons, like their tendency to corrode and to wear the manufacturing equipment, and because of their environmental hazards. To overcome these drawbacks manufacturers have tried to assemble substitute packaging materials in the form layered structures, where the properties of each of the layers are intended to support the others to achieve air

and water impermeability, suitable mechanical properties and a possibility to sterilize the package material and its contents by steam or by irradiation.

Steam-sterilizable multilayer materials are disclosed in numerous publications. A typical simple multilayer film fulfilling this technical  
5 requirement consists of three layers: polyolefin/polyamide/polyolefin. The polyolefin layer acts as a water barrier and the polyamide can be both moisture resistant and act as a substantial oxygen barrier. However, this type of film is not sufficiently effective as a moisture barrier. More efficient films are developed in the patent specifications EP 0216 639 and US 4407897.

10 The European patent application EP 0457 648 discloses a more sophisticated type of film with different polymer barrier layers having complementary properties. In applications with extremely rigorous requirements, like storage of materials for parenteral administration in medicine, not even these films are satisfying in terms of oxygen barrier shaping  
15 qualities.

EP 0236 099 discloses a sterilizable seven layer film with oxygen barrier characteristics having the structure A/B/C/D/C/B/A, where A is an outer layer, B is an adhesive layer, C is an intermediate layer, and D is barrier core layer. The barrier core layer, D, is preferably made from ethylene vinyl alcohol  
20 polymer and is surrounded by two moisture absorbing nylon containing moisture absorbing layers C. The outer layers A, preferably consist of a copolymer of a polyolefin, such as a polyethylene with an unsaturated carboxylic acid or acid anhydride. The moisture absorbing nylon layers, C, will however, include nylon 6, which makes the film unsuitable for medical  
25 applications due to the risk of an eventual caprolactam release which is regarded as a hazardous contribution to parenterally administerable fluids. Nylon containing films also have a tendency to become opaque after heat sterilization which can give the resulting product an undesired appearance. Besides these drawbacks, the films of EP 0236 099 seem to be excessively stiff  
30 for convenient handling and manufacturing and articles made from the film will not be easy to open because that there will not be any peel effect between the outer layers A.

The abstract of the Japanese patent application 3087254 reveals a laminate with good oxygen barrier properties composed a copolymer  
35 polyamide layer containing structural units from meta-xylene polyamide, a polyolefin layer and/or an EVOH layer. This film will, however suffer from the disadvantage of becoming opaque after autoclavation and it will also lack the peel effect between its outer layers.

Consequently, there is still a great demand for improved steam sterilizable multilayer materials with very low oxygen permeability for packaging perishable medical and/or nutritional fluids for parenteral administration in a single primary package with excellent transparency.

5

#### Description, summary and objects of the invention

The invention intends to provide a multilayer film, which is substantially impermeable to oxygen and autoclavable, while having flexible properties suitable for further processing and manufacturing to packages, containers and other shapes to be filled with oxygen sensitive and perishable goods, as well as having the benefit of a high aesthetical value, due to its retention of transparency after autoclavation.

The invention is also directed to flexible containers or medical packages containing medical or nutritional material made from the novel multilayer film, as well as processes for their manufacture and the use of the novel film for the manufacture of such articles.

A further object of the invention is a process for the preparation of the multilayer film by sequentially laminating together the different layers.

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The multilayer film is most readily described by the general sequential palindrome formula A-B-C-D-C-B'-A', wherein each capital letter symbol corresponds to a unique layer of the film.

The layers are all made of polymeric materials with characteristic chemical and physical properties and are generally described in the following part. The outermost layers A and A' front the environment and the perishable goods inside a container made from the multilayer film. In certain applications, when the multilayer film is used as a wrapping for another container, either A or A' faces a bag or a primary container filled with the perishable goods. The multilayer film will in such cases be formed as an envelope or a secondary container filled with an inert atmosphere and a primary container before sealing.

A and A' shall be made from a moisture resistant material capable of withstanding both water vapour and liquid water. These layers can be made from the same or different polyolefines or PET (polyethylene-terephthalate) or copolymers of PET. Preferred polyolefines are polyethenes and polypropylenes with moisture barrier qualities. It is especially preferred to select polyolefines which form a weak seal welding with each other so that peelable contact surfaces will be formed when autoclaving the film. In such cases the layers A

35

and A' shall be made from polymers compatible with each other, so molecules in their contact surfaces can interdiffuse under the influence of heat.

The one of layers A or A' which faces the environment can be removed in a special embodiment of the invention, to further increase the flexibility of the multilayer film, and to provide a surface suitable for welding. In this case the subsequent adhesive layer B will also be removed.

The layers B and B' are adhesive layers or tie-layers providing adhesive bonding between layers A and A' and layers C. The nature of such a layer can be easily determined and chosen by anyone aware of the polarity of layers A and A' and C. For example, B must be a significantly hydrophilic polymer if the other fronting layers are hydrophobic.

The layers C are made from polymers with moisture absorbing qualities and are substantially impermeable for oxygen, thus providing a barrier for oxygen. Especially suitable polymers are found among aromatic polyamides or derivatives or copolymers thereof which can absorb moisture and increase their density and thereby substantially contribute to the oxygen barrier. It also an important requirement that the polyamides are totally biocompatible and not release caprolactams and other potentially hazardous compounds to the stored materials.

The layer D consists of poly(ethylene)-vinyl alcohol (EVOH), which is a material with excellent oxygen barrier qualities as long as it is dry. The EVOH-layer has hydrogen bondings between its hydroxide molecules which will be destroyed by penetrating water molecules, so that oxygen can leak through the layer and its barrier function decays rapidly.

The multilayer film with layers assembled with layers according to above, will provide a surprisingly effective oxygen and moisture barrier both during autoclavation at about 120°C and during storage for the protection of perishable material such as parenteral infusion fluids.

The inventive multilayer film is constructed especially to prevent the EVOH from losing its effect as an oxygen barrier. EVOH, will as previously explained, be an excellent barrier for oxygen in a dry shape.

In previous applications of EVOH, such a film is bonded to a moisture protecting layer of for example polyolefines. The protecting polyolefin layers are sufficient for use under normal conditions, but autoclaving leads to an increase in oxygen penetration which will cause a permanently decreased oxygen barrier quality of the EVOH. Besides that, the autoclaving conditions will lead to a whitening effect which deteriorates the transparency of the film.

According to the present invention the EVOH-layer therefore is surrounded with two layers of a polyamide including aromatic groups (or a

derivative or a copolymer thereof) acting as a moisture absorbent which will absorb water corresponding to the dynamically cycle of the sterilisation in an autoclave. Together with the water resistant layers A and/or A' and the adhesive layers B and/or B', the multilayer film is an optimally assembled film, balancing the kinetics of the steam sterilisation. It means that the EVOH-layer will be protected from water, because water will never have the opportunity to pass the protective layers A and/or A' and C.

The layers C, consisting of an aromatic polyamide (or a derivative or copolymer thereof), both contribute to the oxygen barrier and to the moisture barrier, because of its moisture absorbing quality.

An advantage with the multilayer film according to the present invention is that the specifically selected layers C is that pure EVOH can be used without any compatibilisers, such as nylon, which lead to decreased risks for migration effects during the storage of fluids.

Another advantage compared to conventional films made from polypropylene/EVOH/polypropylene is that the drying step becomes superfluous. The novel films will immediately provide an excellent oxygen barrier after autoclavation and not be subjected to irreversible barrier losses.

The layers A and/or A' are essentially moisture barriers, preventing water to reach the EVOH-layer through the polyamide layers, preferably chosen to form weak seal weldings when heated to form peelable surfaces.

The inventive multilayer film material can be assembled with conventional processing methods as coextrusion or laminating. The conditions for manufacturing process of the film will vary with the materials used as layer components, but can easily be found out by persons skilled in the art. The multilayer film material according to the invention is also easy to process into hollow shapes as sealable, flexible or collapsible containers packages, bags or pouches etc. by conventional means and methods.

Medical packages manufactured from the film will preferably contain sterilizable, but perishable goods, in the form of fluids or solid material to be mixed with such fluids. The goods stored in such packages are intended to be administered parenterally or enterally for therapeutical and/or nutritional purposes.

Examples of such fluids or materials are lipid emulsions, amino acids, glucose and other carbohydrates, vitamins, electrolytes, trace elements or any mixture thereof. These components may be stored together or stored separately in a multi-compartment package prepared from the inventive multilayer film. The medical packages according to the invention can be aseptically filled with the fluids or materials mentioned above and will thereafter be sealed by

conventional sealing means e.g. welding and finally subjected to heat sterilization in an autoclave.

In other applications, for example when especially heat sensitive and perishable goods shall be stored, it can be suitable to fill the perishable goods  
5 aseptically in a primary, inner container principally made of one or plural layers of an at least partially oxygen permeable polymer like EVA poly(ethylene)-vinyl acetate), which is sealed and sterilized by irradiation. In other applications can of course the primary, inner container be sterilized by other means such as steam. The primary container is thereafter placed in an  
10 envelope formed by the multilayer film according to the invention, air is evacuated by vacuum generating means and atmospherical pressure restored by an inert gas before sealing the envelope. All types of containers, bags or envelopes disclosed herein can be manufactured as both one-, two- three- or multi-compartment containers provided with means for communication  
15 between the compartments, so their components can be mixed immediately before dispensing the contents of the containers.

#### Detailed description of the invention and preferred embodiments

20 Figure 1 illustrates a schematic cross sectional view of an embodiment of the film according to the invention. The capital letter symbol in the figure corresponds to the symbols and layers used elsewhere in the text.

Figure 2 shows a comparison of weight changes of different multilayered films and a film according to the invention.

25 Figures 3 and 4 show the change in absorbance for products stored in different multilayered films compared to a film according to the invention.

Multilayer films according to the invention described with the general schematic formula A-B-C-D-C-B'-A' will preferably be composed by individual  
30 layers as follows;

The outer water and water vapour resistant layers A and A', of which one optionally could be removed, can be made of polyolefines, polyethyleneterephthalates (PET) or copolymers of PET. Suitable polyolefines are polyethenes and polypropylenes. The polyolefines should be both moisture  
35 resistant and resistant for sterilization by irradiation, examples of such a materials are the polypropylene WB8052C from Neste and various polyethenes. Polypropylene is especially preferred if the multilayer film shall be subjected to steam sterilization, but if sterilization by irradiation is for some reason is desirable, polyethenes are the suitable choice for layers A and A',



since polypropylenes are not sterilizable with irradiation. Copolymers of polypropylenes and polyethenes are also possible to use in these layers.

It is especially preferable to choose such polypropylene qualities that are capable of forming weak weldings between such layers A and/or A', when

- 5 heating the material e.g. during autoclavation. The effect will be a ready peelable surface between such layers A and/or A'. Persons skilled in the technique will not have any difficulties to find suitable materials for the outer layers according to the guidelines presented above.

- 10 The thickness of outer layers A and A' are preferably 20-100  $\mu\text{m}$  and most preferably 45-55  $\mu\text{m}$ .

The adhesive layers or "tie-layers" B will be chosen from materials providing adhesive bonding with both layers A/ A' and layers C. As previously mentioned above, layers B and B' are chosen with respect to the polarity of the surrounding layers, which shall be bonded together.

- 15 Examples of material suitable for binding polyethenes and polyamides together are Dow Prima Cor 16105 and Admer® QF500E, which are polypropylene modified maleic acid anhydrides. The layers B and B' shall be about 10  $\mu\text{m}$  in thickness. If layers A/ A' consist of polypropylene is Admer® QF55IE a suitable choice as a binding layer.

- 20 The layers C consist of moisture absorbent and oxygen barrier shaping aromatic polyamides or derivatives or copolymers thereof and have a preferred thickness of 20-100  $\mu\text{m}$  , most preferably between 30-40  $\mu\text{m}$ .

- One example of a material appropriate according to the invention is made from a composition of 80 % Nyref® MXD-6 from Mitsubishi with a melting point of  
25 245°C consisting of a copolymer of metaxylenediamine and adipidic acid and 20 % of XE 3303 from EMS-Chemie, which is a copolymer of hexamethylenediamine and adipidic acid or a copolymer of adipidic acid, hexamethylenediamine and sepaic acid. Copolymers of the mentioned MXD6 and XE 3303 are also conceivable according to the invention.

- 30 An example of another suitable composition consists of the mentioned MXD6 of grade 6007 and Polyamide 66 (PA66), (a copolymer of hexamethylenediamine and adipidic acid), with less than 1.3 in relative viscosity. It is also suitable that the polymers of layers C include an aromatic acid having two acid groups combined with an aromatic amine having two amino groups.

- 35 The principal oxygen barrier layer D of the multilayer is made of polyethylene vinylalcohol (EVOH) with a thickness of 2-40  $\mu\text{m}$ , preferably about 20  $\mu\text{m}$ . The molar ethen concentration in the EVOH can vary from 0-80%

(0% means PVOH, polyvinyl alcohol), preferably between 10-50%. An appropriate quality for this layer is BX220 from Dupont with a molar ethene concentration of 33%.

A preferred embodiment of the multilayer film is polyethen

- 5 (A)/adhesive layer made of Dow Prima Cor 16105 (B)/ layer made of 80% MDX-6 and 20% of XE 3303 (C)/ layer of the EVOH BX 220 (D)/ same as previous (C)/ same as previous (B)/ same as previous (A). For the exact definitions of the components of the layers reference is made to the text above.

- 10 The examples of the components of the layers are not intended to be limiting. Any person skilled in the art of polymer materials can easily find appropriate and well functioning alternatives to the components exemplified in this text within the scope of invention as it is defined by the claims.

- 15 The following studies intend to compare the oxygen permeability, the water permeability and the material weight before and after autoclaving between the inventive multilayer film and other film materials.

The seven tested film materials are:

Film 1 : polypropylene (PP) / EVOH; 30% ethene / polypropylene (PP)

Film 2 : PP / EVOH; 44% ethene / PP

- 20 Film 3 : PP / polyamide : XE 3303 (PA) / PP

Film 4 : Polyethen (PE) / PA (as in Film 3) / PE

Film 5 : PE / polyamide : 80% MXD6 and 20% XE 3303 (PA) / EVOH; 33% ethene / PA (same) / PE.

Film 6 : PP / PA (polyamide 6) / a copolymer containing EVOH / PP

- 25 Film 7 : Polyethyleneterephthalat (PET) / glass / PET / PP

The adhesive or "tie-layers" between layers of the exemplified films have not been included in the schematic comparison above. For information about the polyamide materials in Films 3-5, see the detailed description above.

- 30 Film 5 is an example of a multilayer material according to the present invention.

Films 1-5 have been manufactured by Wihuri Oy Wipak Medical and Films 6-7 are supplied by Soplaril S.A.

- 35 Film 6 is an example of a material disclosed in the European Patent Application EP 0457 648.

Table 1 shows the oxygen permeability measured in cubic centimetres per square meter, day and bar for Films 1-7 at different temperatures and different relative humidity.

Table 1

		<u>Permeability (before sterilization)</u>	
		Ox. 23°C/60%RH cc/m <sup>2</sup> ,day,bar	Ox. 50°C/>95%RH cc/m <sup>2</sup> ,day,bar
5			
10	Film 1	<0.5	8.50
	Film 2	5.00	
	Film 3	38.00	195.00
15	Film 4	37.00	175.00
	Film 5	0.50	4.50
20	Film 6		6.00
	Film 7	0.84	5.00

25 The results from Table 1 indicate that Film 5, prepared according to the present invention, has the best oxygen barrier properties of the compared multilayered films.

Figure 2 presents weight changes before and after autoclavation of pouches made from Films 1 and 3-7. The pouches were weighed before and after autoclavation, wrapped around an inner bag and once again autoclaved. 30 The inner bag was removed and the pouch wiped dry. The pouches were weighed again after 1 hour, 24 hours and one week, respectively.

The results from this test show that Film 5 according to the present invention absorbs more moisture and retains it much longer (has lower weight reduction) than the other films. This can be explained by the double polyamide 35 layers of Film 5 absorbs more water and holds it longer.

It is however, surprising that this film has such a low oxygen permeability. This phenomenon can be explained by that the PA-layers absorb so much moisture during the autoclavation that it never reaches the EVOH in the interior of the film.

Figures 3 and 4 show the absorbance measured at 430 nm after six weeks and three months storage of Vamin 18® (an amino acid mixture useful in parenteral nutrition) in containers manufactured from Films 1 and 3-7 and in comparison to traditional storage materials as glass bottles and aluminium foil.

- 5 The absorbance value will be a measure of the oxygen penetration of the film. The increase in absorbance is derived from oxygen dependent dimerization of certain amino acids in Vamin 18®.

- 10 As shown in Figures 3 and 4, Film 5 according to the invention has superior properties regarding oxygen penetration compared to the other film materials and comparable to the traditional materials.

- 15 The advantageous results of the film according the invention must be credited to the surprisingly successful efforts to combine the properties of the different layers. Especially in terms of providing an efficient moisture barrier with moisture absorbent properties surrounding the principal oxygen barrier layer D of EVOH. The inventive multilayer film can be seen as effort to provide an ideal environment for layer D, so its oxygen barrier properties are constant even during and after autoclavation.

## Claims

1. An autoclavable multilayer film assembled of thermoplastic materials,  
capable of being processed into hollow shapes and useful for the packaging of  
5 oxygen sensitive goods characterized in that it consists of the sequential layers  
A-B-C-D-C-B'-A' wherein

A and A' are layers substantially resistant for water and water vapour;

- 10 B and B' are layers providing adhesive bondings between layers A and A' with  
C;

- C is a layer of a moisture absorbing polymer substantially impermeable for  
oxygen which contains an aromatic polyamide or a derivative or a copolymer  
15 thereof;

D is a layer consisting of polyethylene-vinyl alcohol (EVOH) with a molar  
ethene concentration between 0 to 80%

- 20 and wherein one of A or A' and one of B or B' may optionally be removed.

2. A film according to claim 1 characterized in that the layers A and/or A' are  
made of polyolefines, polyethyleneterephthalates or copolymers  
polyethyleneterephthalates.

- 25 3. A film according to claims 1 or 2 characterized in that layer C contains at  
least one aromatic polyamide which is a copolymer of hexamethylenediamine  
or metaxylenediamine.

- 30 4. A film according to claims 1 or 2 characterized in that layer C contains at  
least one aromatic polyamide which contains an aromatic acid having two acid  
groups and an aromatic amide having two amino groups.

- 35 5. A film according to any of claims 1-4 characterized in that the layers A  
and/or A' are made of polyethen or polypropylene or copolymers thereof.

6. A film according to any of claims 1-5 characterized in that the molar ethene  
concentration of the EVOH in layer D is between 10 to 50%.

7. A film according to any of claims 1-6 characterized in that layers A and A' have a thickness between 20 to 100  $\mu\text{m}$  each, preferably between 45 to 55  $\mu\text{m}$ ; layers B and B' have thickness between 2 to 30  $\mu\text{m}$  each, preferably between 5 to 25  $\mu\text{m}$ ; layers C have a thickness between 20 to 100  $\mu\text{m}$  each, preferably between 30 to 40  $\mu\text{m}$ ; layer D has a thickness between 2 to 40  $\mu\text{m}$ , preferably between 15 to 25  $\mu\text{m}$ .
8. A film according to any of claims 1-7 characterized in that it is transparent after autoclavation and yet retains its oxygen barrier capacity.
9. A flexible container manufactured from the multilayered film according to any of claims 1-8.
10. A flexible container according to claim 9 characterized in that it contains sterilizable medical or nutritional fluids .
11. A flexible outer package for medical and/or nutritional use characterized in that it is manufactured from the multilayered film according to any of claims 1-8 and that it contains fluids to be administered parenterally optionally in a primary, inner package.
12. Process for the manufacture of a medical package according to claim 11 characterized in that the package is aseptically filled with the fluids, sealed with sealing means and subjected to steam sterilization.
13. Use of a multilayered film according to any of claims 1-8 for the preparation of an autoclavable, flexible container which contains medical or nutritional fluids.

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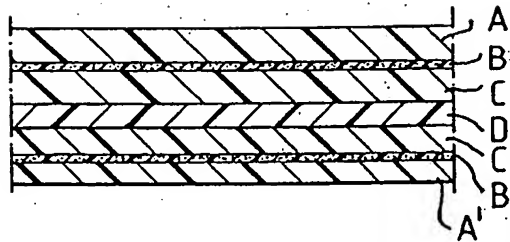


Figure 1

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## WEIGHT CHANGES OF OVERWRAP

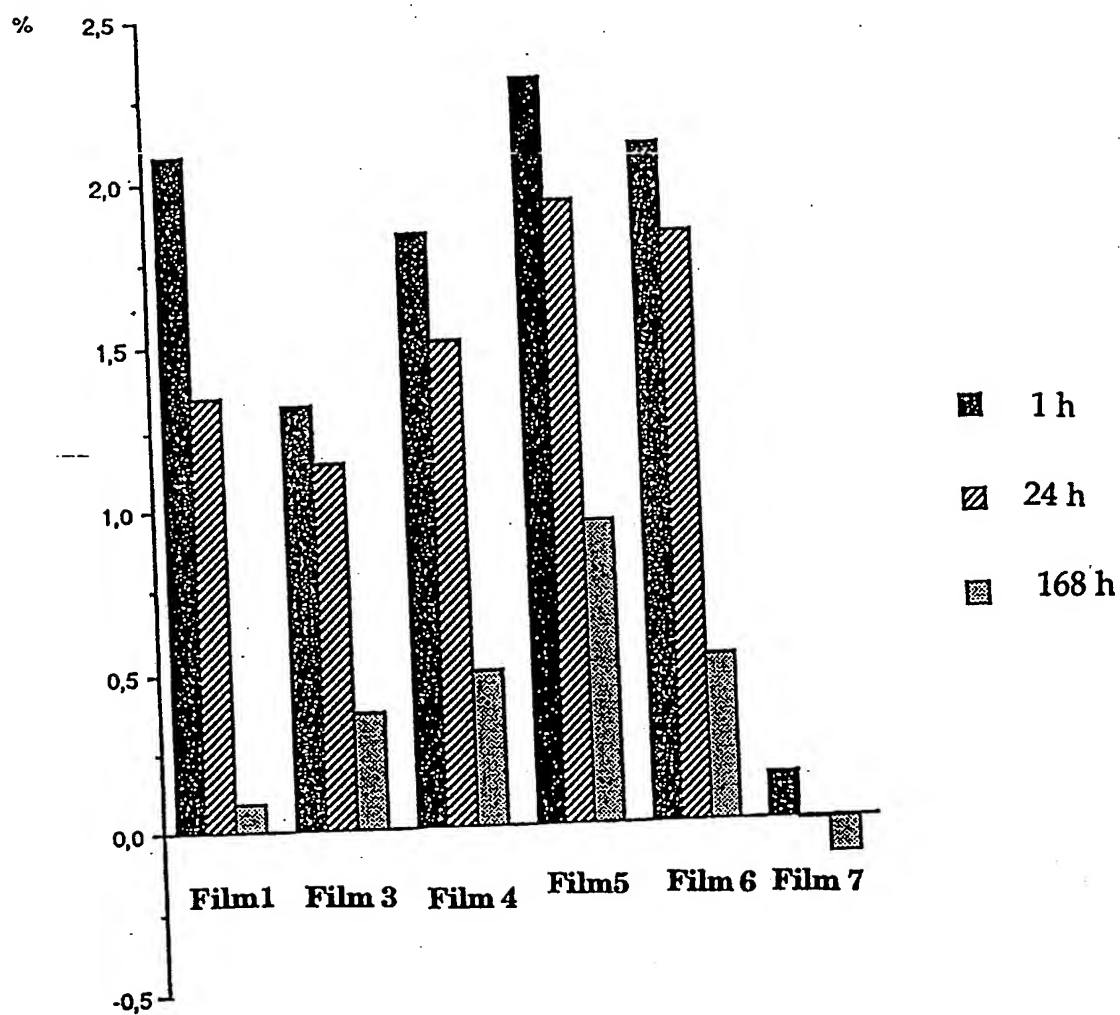


Figure 2



3/4

Abs 430 nm

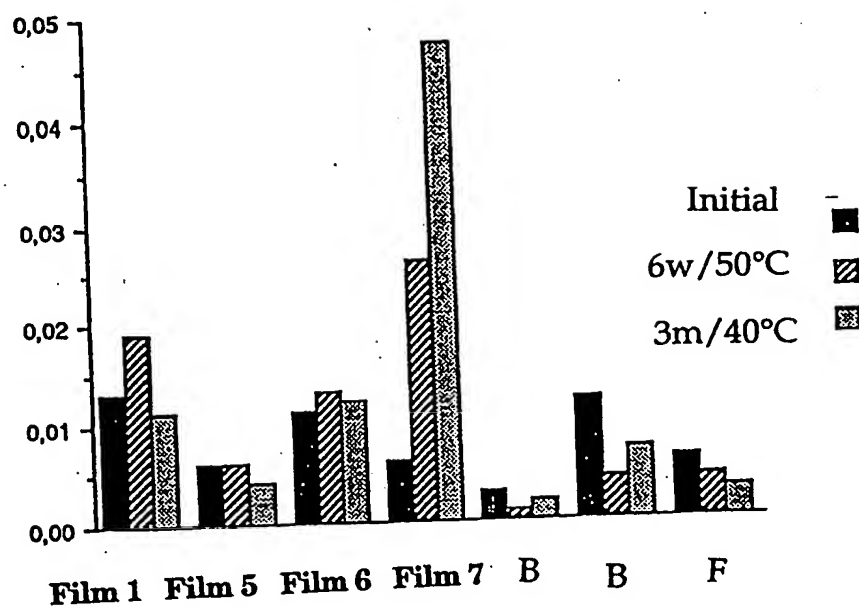


Figure 3

SUBSTITUTE SHEET

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Abs 430 nm

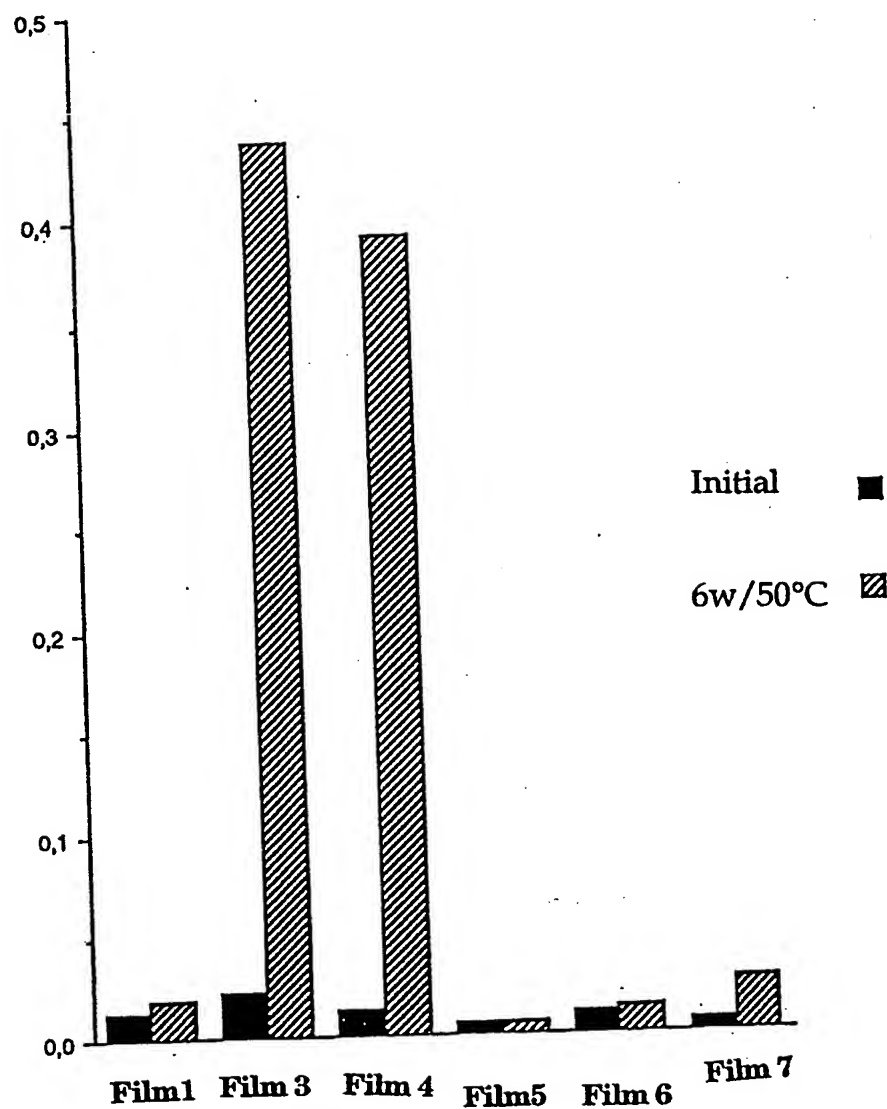


Figure 4

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 94/00138

## A. CLASSIFICATION OF SUBJECT MATTER

IPC<sup>5</sup>: B32B 27/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>5</sup>: B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CLAIMS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP, A2, 0236099 (W.R. GRACE & CO.), 9 Sept 1987 (09.09.87), page 13 - page 16, abstract  --	1-13
Y	Dialog Information Services, file 351, World Patent Index, Dialog accession no. 008648439, WPI Acc No: 91-152468/21, ((MITU) MITSUBISHI KASEI CORP), "Laminate with gas barrier properties useful for food packaging - comprises polyamide layer contg. structural units obtd. from M-xylene diamine, isophthalic acid and aliphatic dicarbox- ylic acid; POLYOLEFIN POLYETHYLENE POLYVINYL ALCOHOL", JP 3087254, A, 910412, 9121  -----	1-13

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

24 May 1994

Date of mailing of the international search report

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

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